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THE BONDING IN THE INERT GAS-HALOGEN COMPOUNDS—THE LIKELY EXISTENCE OF HELIUM DIFLUORIDE

Sir:

In 1951, Pimentel discussed the bonding in trihalide ions in terms of a simple molecular orbital description.[1] In this widely ignored paper, the applicability of the bonding scheme to other molecular species was recognized and, in fact, the existence of inert gas–halogen compounds was predicted. "*It is to be expected that a rare gas could form complexes with halogens.*"[1] At about the same time, Hach and Rundle[2] discussed bonding of trihalides in similar terms, though without any reference to possible inert gas compounds.

Since then there has appeared significant support for this molecular orbital description of the trihalides through electric quadrupole resonance studies[3,4] and infrared studies.[5] The quadrupole coupling constants in both ICl_2^- and ICl_4^- confirm the proposal that d orbitals do not contribute significantly to the bonding.

The recent preparation of inert gas compounds has naturally stimulated much interest in their bonding.[6–9] Among these discussions, there has appeared a revival of the molecular orbital description proposed by Pimentel[8,9] and, we feel, the model provides a simple and sufficient basis for explaining the existence of such compounds as XeF_2. The case of extension of the scheme to such compounds as ICl_4^- and XeF_4 has been amply pointed out by others[4,5,8,9] and need not be reproduced here.

There is, however, one other aspect of the molecular orbital description offered by Pimentel[1] that deserves consideration. The essential similarity of the molecular orbital descriptions of HF_2^- and I_3^- was noted[1] and remarked upon again by Pimentel and McClellan.[10] Experimental support for this connection has also appeared[11] and we are encouraged to explore its implications in reference to inert gas chemistry. In particular, *the compound HeF_2 can be expected to be stable.*

The molecular orbital description of HF_2^-, based upon the halogen axial 2p orbitals and the hydrogen 1s orbital,[1] need not be repeated here and its applicability to the isoelectronic molecule HeF_2 is obvious. We can, however, make some comparisons between HF_2^- and HeF_2 that may aid in searching for this interesting molecule. A rough estimate of the infrared spectrum of HeF_2 can be based upon that of HF_2^-. The vibrational frequencies and a set of force constants for HF_2^- are shown in Table I.[12] These force constants transferred to HeF_2 lead to the predicted frequencies shown in the second row of Table I. We feel, however, that the spectrum of XeF_2 is relevant here. Smith has concluded[13] that the ratio f_{rr}/f_r is much smaller for XeF_2 than for the trihalide ions. We do not share his view that this difference vitiates the molecular orbital bonding description, for a reasonable rationale can be formulated to explain it. The molecules XeF_2 and ICl_2^-, though isoelectronic (in bonding electrons), involve quite different formal charge distributions. The proposed molecular orbitals tend to place somewhat less than one electron charge on the central atom and somewhat more than $1^1/_2$ electron charges on the terminal atoms. In the case of ICl_2^-, the formal charge implication is that the excess charge of the ion is distributed on the chlorine atoms and the iodine atom has a charge near zero. The case of XeF_2 contrasts since the central atom must have a significant positive formal charge to balance the negative charge placed on the terminal atoms. This difference can be expected to tend to strengthen the bond somewhat because of the electrostatic attractions, raising f_r.[14] At the same time, the interaction force constant should be reduced, because an asymmetric displacement is no longer energetically favored over a symmetric displacement. In the symmetric mode, the terminal atom repulsions that tend to raise the energy are counteracted by the central atom positive charge.

Table I

The Vibrational Potential Function and Frequencies of HF_2^- (experiment) and HeF_2 (predicted)

	Frequency, cm.$^{-1}$ ν_1 (Raman active)	ν_2 (Infrared active)	ν_3 (Infrared active)	Bond length, Å	Force constant[a] f_r	f_{rr}	f_α
HF_2^-	600	1230	1425	1.13	2.31	1.72	0.28
HeF_2	600	640	743	1.13	2.31	1.72	.28
HeF_2	585	673	1600	1.08	3.47	0.35	.28

[a] f_r = bond stretching force constant (in millidynes/Ångstrom); f_{rr} = bond stretching interaction force constant (in millidynes/Ångstrom); f_α = angle bending force constant (in millidyne-Ångstrom/radian).

In view of these considerations, we feel that a more educated guess of the force constants for HeF_2 is possible. In the last row of Table I, we propose a more likely potential function (and an appropriately shortened bond length) together with the implied frequencies.

Though the two sets of predicted frequencies are discordant, they show that the infrared absorptions should fall in a readily accessible region. A search for this species, HeF_2, is in progress here.

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(14) A prototype effect is noted in the successively shorter bond lengths of ClO_2^- (1.64 Å.), ClO_3^- (1.57 Å.) and ClO_4^- (1.50 Å.), which also can be associated with the accumulating formal charge on the central atom.

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